

### VI.D.3 Hydrogen Storage in Novel Molecular Materials

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#### Objectives

- Develop and demonstrate reversible CH<sub>4</sub>, H<sub>2</sub>O - based cost-effective hydrogen storage clathrate materials.
- Demonstrate at least 7 wt% materials-based gravimetric capacity and 50 g H<sub>2</sub>/L materials-based volumetric capacity by the end of 2008.
- Achieve refueling time 1 kg H<sub>2</sub>/minute by the end of 2008, with the potential to meet the DOE 2010 system-level targets.

#### Technical Barriers

This project addresses the following On-Board Hydrogen Storage technical barriers outlined in the Hydrogen, Fuel Cells and Infrastructure Multi-Year Research, Development and Demonstration Plan:

- A. Cost
- B. Weight and Volume
- C. Efficiency
- D. Durability
- E. Refueling Time

#### Technical Targets

This project is conducting fundamental studies of inorganic H<sub>2</sub> clathrates (H<sub>2</sub>O- and CH<sub>4</sub>- based). Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the DOE 2010 hydrogen storage targets, especially cost, specific energy, energy density, environmental cleanliness, and safety of hydrogen storage.

## Approach

Clathrates with very high  $H_2$  contents were synthesized by us in diamond anvil cells at high pressure (P) and low temperature (T); clathrate formation and hydrogen release are spontaneous.

- **Challenge:** Extend the P-T stability field to near ambient P and T.
- **Approach:** Stabilize clathrates with additional guest molecules (promoters).

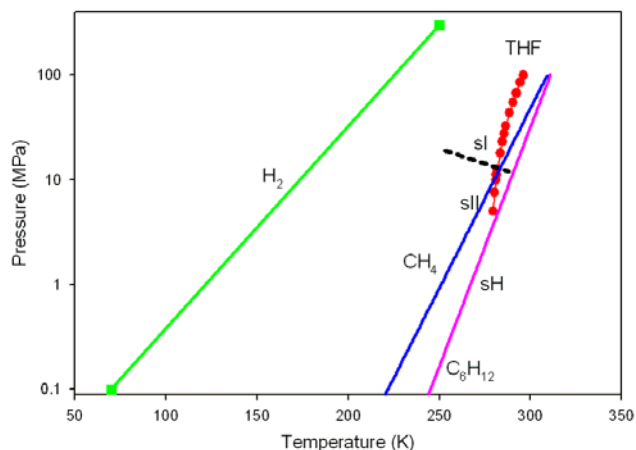
We will be testing at least 5 promoters for each of two systems ( $H_2O$ ,  $CH_4$ ) and will achieve reproducible measurements of storage capacity.

We will demonstrate the material with the reversible capacity  $> 3$  wt% by the end of 2005. (Promoters: Tetrahydrofuran - THF, organic molecules, acids, argon). Reversible hydrogen storage with 4% weight capacity has been already demonstrated for THF- $H_2O$  sII clathrate at 270°K and 12 MPa by H. Lee et. al. (*Nature* 434, p. 743, 2005). A preliminary phase diagram for  $H_2$  hydrates is shown in Figure 1. Addition of THF moves the stability line for  $H_2$ -sII clathrate to nearly room temperature at  $P > 50$  MPa. The stability line is strongly nonlinear, suggesting that THF-stabilized  $H_2$  clathrate could exist above 250°K at ambient pressure. The sH clathrate with methylcyclopentane ( $C_6H_{12}$ ) could be another candidate for  $H_2$  storage, due to even larger cages than in sI and sII clathrates.

We will extend  $H_2$ - $CH_4$ - $H_2O$  clathrate stability field measurements to lower temperatures and lower pressures to select two compositions viable for a reversible capacity of  $> 5$  wt% above the temperature of the dry ice -78°C (by the end of 2006). Theoretical modeling using classical molecular dynamics and quantum Monte Carlo simulations will be used to understand the effect of multiple  $H_2$  occupancy in small and large cages on clathrate stability. Standard calculation methods based on Gibbs energy minimization technique (E. D. Sloan, *Nature* 426, 2003) are not directly applicable to a multiple occupancy scenario.

By the end of 2007 we plan to optimize hydrogen storage materials based on  $H_2$ - $CH_4$  and  $H_2O$  clathrates to reach materials-based gravimetric capacity 6 wt%, materials-based volumetric capacity 40 g  $H_2$ /L, and to allow refueling time 0.5 kg  $H_2$ /minute.

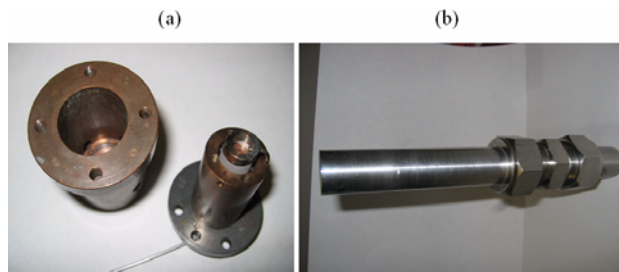
Further optimization of clathrate materials will be aimed at materials-based gravimetric capacity 7 wt%, materials-based volumetric capacity 50 g  $H_2$ /L, and a refueling rate of 1 kg  $H_2$ /minute (end of 2008).



**Figure 1.** Stability Ranges of  $H_2$ -(THF) -  $H_2O$ ,  $CH_4$  -  $H_2O$  Clathrates. Blue line – extrapolated stability line for  $CH_4$ - $H_2O$  (sI & sII clathrates); Dashed line separates stability fields of sI and sII clathrates; Red circles –  $H_2$ -THF- $H_2O$  clathrate (Florusse et al., *Science* 306, p.469, 2004); Green squares and line – stability line of  $H_2$ - $H_2O$  sII clathrate (W. Mao et. al.); Magenta – extrapolated sH  $C_6H_{12}$ - $H_2O$  clathrate stability line

## Accomplishments

- Achieved 33% hydrogen storage capacity by weight in  $(\text{H}_2)_4\text{CH}_4$  at 360 MPa, 86 K. Preliminary results have been published by W. L. Mao, V. V. Struzhkin, H-k. Mao, and R. J. Hemley, "P-T stability of the van der Waals compound  $(\text{H}_2)_4\text{CH}_4$ ", *Chem. Phys. Lett.* 402, 66-70, 2005.
- Large-volume cells for Raman, IR, XRD, and neutron spectroscopy have been designed and manufactured (Figure 2). The Raman cell is designed for the 0.1-0.3  $\text{cm}^3$  volume; the neutron cell accommodates up to 10  $\text{cm}^3$  of the clathrate material. The cells are designed for <25 MPa. Experimental design involves optimizing the conditions for formation of the clathrate and then cooling the sample to a temperature where the structures are stable at ambient pressures to minimize transportation risks. We were able to retain 680  $\text{cm}^3$  of hydrogen gas in THF-based clathrate sample having less than 10  $\text{cm}^3$  volume, using our neutron large volume cell, and performed inelastic neutron scattering measurements in THF- $\text{H}_2$ - $\text{H}_2\text{O}$  and THF- $\text{D}_2\text{O}$ .



**Figure 2.** Large-volume Cells for Raman, IR, XRD and Neutron Spectroscopy  
 (a) *Modified Diamond Anvil Press for Moderate Pressure Raman and IR Measurements.* This cell can also be used for XRD measurements. The cylinder has a sapphire window, and the assembled cell can be clamped using screws. The piston assembly has a sapphire window and a copper spacer (sealed with teflon or indium rings) connected to a high pressure capillary.  
 (b) *Moderate Pressure Neutron Gas Cell.* Aluminum sample container is exposed to the neutron beam. Aluminum is used because of the low scattering cross section that it possesses, making it transparent to neutrons. Not shown is the capillary and valve assembly that connects to it to allow *in situ* experimental adjustments.